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Japanese Kokai Patent Application
No. Hei 4[1992]-100976

FABRICS TREATED WITH MODIFIED SILK FIBROINS AND METHOD
FOR THEIR MANUFACTURE

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FABRICS TREATED WITH MODIFIED SILK FIBROINS AND METHOD
FOR THEIR MANUFACTURE
[Henseikinu fiburoin de kaishitsukako shita sen-I kozobutsu
oyobi sono]

Inventors: Kiyoshi Otoi, Osami
Yamamoto

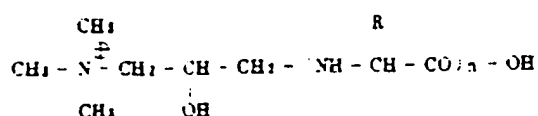
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[There are no amendments to this patent.]

Claims

1. Fabrics treated with quaternary trimethylammonium-modified silk fibroins; the quaternary trimethylammonium can be represented by general the formula:



(wherein R is the side chain of amino acid which constitutes the silk fibroins and n is the average degree of polymerization (i.e., the number of monomer units incorporated in one chain) and it is 100-1000)).

2. Method for manufacturing fabrics treated with quaternary trimethylammonium-modified silk fibroins, characterized in that an aqueous silk fibroin solution (concentration: 3-20 wt%) is hydrolyzed to an average degree of polymerization of 100-1000 (average molecular weight: 8500-85,000) by an acid, an alkali, or a proteolytic enzyme, and while the reaction system is maintained alkaline, (3-chloro-2-hydroxypropyl)trimethylammonium chloride is added dropwise to give an aqueous quaternary trimethylammonium-modified fibroin solution; then fabrics are immersed in the thus obtained aqueous quaternary trimethylammonium-modified fibroin solution, and then the fabrics are dewatered to the specified pickup and if necessary the fabrics are subjected to wet heat treatment.

*cpd → not
polymer*

Detailed explanation of the invention

Industrial application field

The present invention pertains to an improvement of the appearance and hand of fabrics. More precisely the present invention pertains to fabrics treated with quaternary trimethylammonium-modified fibroins and a method for their manufacture.

Prior art

Silk has a deep luster, good appearance and hand, elegant drape properties, etc., that are the objective of other fabrics and has a unique noble and elegant quality, therefore it is called the queen of fabrics.

Therefore spinning methods and processing methods have been proposed which can impart the characteristics of silk to fabrics other than silk, and some of the methods have been put to practical use. As for the processing methods, for example, softening by an alkali treatment of polyester fibers and enzyme treatment of cellulose fibers for weight reduction and softening, and for a widely used method, the processing of urethane resin, silicone resin, or amino acid resins was proposed for imparting softness and drape properties.

On the other hand, as a method for treating fibers with an aqueous silk fibroin solution, it was described in Japanese Kokoku Patent No. Sho 57[1982]-13670 that films made of silk fibroins were formed on the surface of fibers for improving the drawback of inferior drape properties and the appearance and

hand caused by the inferior stiffness of yarns to [equal] that of raw silk, and it was described in Japanese Kokoku Patent No. Sho 63[1988]-8237 that a method was proposed for manufacturing silk fibroin-treated spun acrylic yarns in which at least a portion of the space between fibers of spun acrylic yarns was filled with silk fibroin for improving the stiffness, stretchability, and resilience of spun acrylic fibers.

Problems to be solved by the invention

However, when we look into the methods weight reduction, softening processing and the surface treatment of synthetic resins are strictly processes using foreign matter, therefore materially their effect and durability are not satisfactory.

In the above-mentioned Japanese Kokoku Patent No. Sho 57[1982]-13670 and Japanese Kokoku Patent No. Sho 63[1988]-8237 (hereinafter referred to as "two patents"), in the proposed modification using aqueous silk fibroin solutions, the common point between them is that the objects treated are both spun yarns. In the case of spun yarns, there are many stable voids between fibers, therefore by capillary phenomenon, a lot of processing solution can be drawn into the voids and held stable. On the contrary in the case of filament yarns, the structure is simple so the voids are few and easily change shape, therefore the amount of processing solution that can be drawn in by the capillary phenomenon is small and easy drips some off so that [the yarns] were not practical (reference: 31st line-45th line, p. 2, Japanese Kokoku Patent No. Sho 63[1988]-8237).

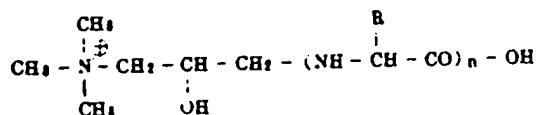
In the case of the above-mentioned two patents, the aqueous silk fibroin solution can be drawn even into the voids between the yarns therefore it is limited to the processing of yarns. Namely when only silk fibroin treatment based on the two patents is merely carried out for the fabrics, by yarn-yarn adhesion, the fabrics become coarse and hard. The above-mentioned statement means that for polyester and nylon, whose regulations for yarn quality are strict and the price of the yarns is inexpensive [sic], the execution of a mere silk fibroin processing, whether filament or cloth, is unsuitable.

Furthermore even limited to the processing of spun yarns, in the case of the above-mentioned two patents there are problems of the variation of the degree of the processing caused by the amount of pickup of the aqueous silk fibroin solution, and also nonuniform squeezing, so the problem of nonuniform dyeing occurs. It is necessary to improve the durability of the luster, appearance and hand, moisture absorption and moisture retention.

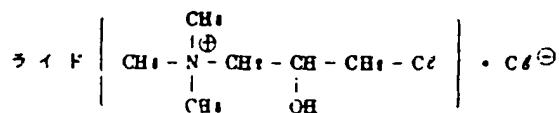
The object of the present invention is to impart uniformly the luster, appearance and hand, moisture absorption and moisture retention of silk to fabrics such as silk, cotton, wool, polyester, nylon, acrylic fabrics, etc., and especially to fabrics made of long fibers, and to provide fabrics having excellent durability for these properties. Another object is to provide a method for manufacturing such fabrics, especially manufacture easily and inexpensively.

Means to solve the problems

The present inventors considered the above-mentioned problems of the prior art and thus carried out an extensive study on the physical properties of silk fibroins and their derivatives, mainly the practicality of treatment of long-fiber fabrics, and as a result completed the present invention. Namely, the present invention pertains to fibers treated with quaternary trimethylammonium-modified silk fibroin; the quaternary trimethylammonium compound can be represented by the following general formula:



(wherein R is the amino acid side chain which constitutes the silk fibroin, n is the average degree of polymerization and is 100-1000), and the present invention is characterized in that an aqueous silk fibroin solution (concentration: 3-20 wt%) is hydrolyzed with an acid, an alkali, or a proteolytic enzyme to an average degree of polymerization 100-1000 (average molecular weight 8500-85,000), then while the reaction system is maintained at an alkaline pH, (3-chloro-2-hydroxypropyl)trimethylammonium chloride (hereinafter referred



to as CTA) is added dropwise, then fibers are immersed in the thus prepared quaternary trimethylammonium-modified silk fibroin aqueous solution, then the fibers are dewatered to a specified pickup and if necessary the fibers are subjected to wet heat treatment.

The problem of modification of fibers by treating with an aqueous silk fibroin solution is that there is neither a chemical nor electrostatic strong adhesion between the objective fibers and the silk fibroin adhered in processed yarns of nylon and polyester, the amount of silk fibroin adhered is small, and if a frictional force is applied to them, the adhered powdery silk fibroin can come off easily. In the case of fabrics, if the squeeze is small (wringing of wet fabrics for dewatering is weak) then due to the yarn-yarn adhesion the appearance and hand become poor. It is necessary to carry out strong dewatering to prevent yarn-to-yarn adhesion, however in this case because there is no selective adsorption between the objective fibers and the silk, even the aqueous silk fibroin solution in the voids of the fibers is removed so that it is restored to its untreated state. Even in the case of spun silk and spun acrylic yarns, if they have selective adsorption power, nonuniform processing can be prevented by strong dewatering.

However generally speaking, fibers in an aqueous process solution carry a minus zeta potential. Therefore if we want to

make the silk fibroin be adsorbed strongly by the fibers with durability, it is possible to do so by modifying the silk fibroin to change positively (i.e., charged with a positive charge) (reference: Kagaku Benran, Ogokagaku-hen [Applied Chemistry Section, Chemistry Handbook], p. 1209, 1986, Maruzen Book Company). We found such an example in silk peptides, however we could not find a method for efficiently cationizing aqueous silk fibroin solutions which are heretofore unstable to acids and alkalis.

The present inventors conducted hydrolysis of aqueous silk fibroin solutions (concentration 3-20 wt%) with acids, bases, and proteolytic enzyme to an average degree of polymerization 100-1000 (average molecular weight 8500-85,000), then by maintaining the reaction systems in alkaline condition,, added CTA dropwise to conduct a reaction and unexpectedly found that quaternary trimethylammonium-modified silk fibroins were formed easily and in good yield and the silk fibroins were cationized, then using it as a processing solution to immerse fibers in it, then the fibers were dewatered to a specified pickup, and if necessary when it was wet-heated, the silk fibroins were efficiently adsorbed by the fibers, thereby the luster, appearance and hand, adsorption of moisture, and retention of moisture of the treated fibers were remarkably improved to give a silk-like appearance and even after laundering and friction, these excellent properties were not deteriorated.

The silk fibroin raw materials used in the present invention can be obtained by removing sericin from cocoons, raw silk, cocoon waste, raw silk waste, bisu, boiled silk, fabric wastes, bourette, etc., using a common method and if necessary

in the presence of an activator in warm water or in the presence of an enzyme in warm water and then dried.

Examples of the solvent used for silk fibroins include aqueous copper-ethylenediamine solution, copper hydroxide-aqueous ammonia solution (Schweitzer's reagent), copper hydroxide-alkali-glycerine aqueous solution (Roe reagent), aqueous solutions of lithium bromide, aqueous solutions of chlorides, nitrates or thiocyanates of calcium, magnesium, or zinc, and aqueous solution of sodium thiocyanate. However from the viewpoints of cost and use, the use of chlorides or nitrates of calcium or magnesium is preferable. The concentration of these aqueous solutions to be used depends on the type of solvents, temperature, etc., however the concentration of the metal salts is usually 10-80 wt%, preferably 20-40 wt%. They can be dissolved even at 80 wt% or greater, however there is no essential difference in the silk fibroin aqueous solution formed and moreover it is not economical.

The silk raw material after scouring is added to a solvent of the above-mentioned solutions and uniformly dissolved at 60-95°C, preferably 70-85°C in a kneader, however the liquor ratio is usually 2-50, preferably 3-30.

If we want to obtain a high-purity silk fibroin aqueous solution from the obtained dissolved silk fibroin solution, it is necessary to subsequently conduct dialysis. The dialysis can be carried out using a dialyzer equipped with a hollow fiber and a dialysis membrane represented by cellophane membranes, thereby the above-mentioned salts can be removed almost completely. In this case it is necessary to specify the amount to be dialyzed and the area of the dialysis membrane for minimizing the molecular weight distribution of the silk fibroins and adjusting

the proportion of α structure silk fibroin to 50 wt% or greater; namely, conduct desalting using a multilayer membrane structure or a bundle of hollow yarns satisfying the following formula:

$$\text{Membrane surface area (cm}^2\text{)}/\text{priming capacity (cm}^3\text{)} \geq 10$$

(where the priming capacity is the inner volume of the dialysis tube or the inner volume between the membranes).

When the above-mentioned value is less than 10, separation by the membrane cannot be carried out rapidly so the retention time in the dialyzer becomes long, therefore very often the aqueous fibroin solution thus obtained starts to decompose. In this case the fibroin protein is converted into water-insoluble structure (β -structure) by the decomposition and it is difficult to make it easily soluble in cold water again.

It is especially preferable to control the above-mentioned numerical value to at least 30, more preferably to at least 50 for conducting the present invention smoothly and economically. It is necessary to control the diameter of the hollow yarn to 4 mm or less to satisfy the condition in case a hollow yarn bundle structure is used.

The dialysis liquid obtained in the present invention contains as little as 0.003-0.06 wt% of residual salts, and especially when the diameter of the hollow yarn is about 0.2 mm:

$$\text{surface area of membrane (cm}^2\text{)}/\text{priming capacity (cm}^3\text{)} = 200;$$

and this can be achieved with a retention time in the dialyzer of 10 min, yielding very high-quality aqueous silk fibroin solutions.

In the present invention the concentration of the silk fibroins is not essentially but is preferably 3-20 wt%, and can be concentrated if necessary. If it is less than 3 wt% it is necessary to concentrate prior to reacting with a cationizing agent for increasing the efficiency of the operation, which is not economical, whereas if it is greater than 20 wt%, then the viscosity is too high which is no good for the reaction and operation.

In the present invention, it is preferable to hydrolyze the silk fibroins with natural molecular weight of 300,000-400,000 (reference: continued: Structure of silk yarns, p. 121, 1980, Published by the Faculty of Fibers, Shinshu University) to a degree of polymerization 100-1000 (molecular weight 8500-85,000) for increasing the number of reactive groups (terminal amino group) for reacting with the cationizing agent. If the degree of polymerization is less than 100, the reactivity with CTA is good, however the strength of the film of the silk fibroin adsorbed to the fibers is weak and it has no luster, whereas when it is greater than 1000, the number of the terminal amino groups is insufficient, thus the films easily come off laundering.

The acids which can be used for the hydrolysis include inorganic acids such as hydrochloric acid, sulfuric acid, etc., however they are not essential. Examples of alkali that can be used include inorganic alkali such as sodium hydroxide, potassium hydroxide, lithium hydroxide, ammonium hydroxide, etc., however from the points of view of reactivity, economy, and stability, the use of sodium hydroxide and potassium hydroxide is preferable.

The conditions for hydrolysis by acids or alkalis depend on the type of acid and alkali, the average degree of polymerization and the distribution of the degree of polymerization of the objective silk fibroins, however the concentration is usually 0.001-0.1N, preferably 0.05N or less, the temperature is 20-110°C, preferably 30-100°C, and the reaction time is 0.5-48 h, preferably 1-24 h, and then an alkali or an acid is added for neutralization.

Examples of hydrolase which can be used in the present invention include common proteolytic enzymes such as (1) pronase which can be obtained from actinomycetes, (2) a group of enzymes which can be regarded as a mixture of several kinds of proteases such as Prolase obtained from papaya, (3) bromelin, etc., and one or a mixture can be used. The amount of enzyme to be used depends on the type of enzyme, purity of enzyme, reaction conditions, or the average degree of polymerization of the silk fibroins, etc., however usually it is 0.01-1.0 wt%, preferably 0.02-0.5 wt%. In this case the conditions for the hydrolysis depend on the type and concentration of the enzyme used, however usually the pH is 6-9, preferably 8-8.5, the temperature is 20-70°C, preferably 30-45°C, and the reaction is carried out for 0.1-72 h, preferably 0.5-12 h.

In the present invention the silk fibroins which were prepared to have a degree of polymerization of 100-1000 react with CTA to give a quaternary trimethylammonium-modified silk fibroins. Commercially available CTA with a concentration of approximately 50 wt% can be obtained easily and the CTA can be added dropwise to an aqueous silk fibroin solution which was prepared to have the adequate degree of polymerization, thereby

*Carbonic cpd.
reacted to
silk
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fib*

the cationization modification of the fibroins can be carried out easily with a good yield.

In this case it is preferable to maintain the pH of the reaction system at 8-12, preferably 9-11, therefore during the reaction it is necessary to add dropwise an aqueous alkali solution such as sodium hydroxide and potassium hydroxide for neutralizing the hydrochloric acid produced in the cationization modification of the silk fibroins. In an acidic condition the reaction cannot proceed selectively. And if the pH is greater than 12, hydrolysis of CTA and the silk fibroins occurs.

The reaction temperature is room temperature to 80°C, preferably 40-60°C. The higher the temperature, the faster the reaction rate, however for the reaction carried out in an alkaline medium, if the temperature is higher than 80°C, the hydrolysis of CTA and the silk fibroins proceeds, which is undesirable.

The reaction time is 30 min to 1 h during the dropwise addition of CTA, and then it is stirred for 3-4 h and finally it is stirred at 80°C for 30 min to complete the reaction. After the reaction is completed, the reaction mixture is neutralized with an acid, and then the alkali ions are removed by a weakly acidic ion-exchange resin to give a treatment solution of fibers.

In the present invention, though, depending on the objective fibers, the suitable pickup is approximately 50-200% (1/2- to 2-fold the weight of untreated fabrics) and the concentration of cation-modified silk fibroins in the treatment solution is usually 0.5-20%, especially 1.0-10.0% is suitable, thereby the amount adsorbed to the fabrics can be controlled to 0.5-20%.

If it is less than 0.5%, the treatment for obtaining a silky hand is insufficient, whereas if it is greater than 20%, the fibers become hard and coarse.

In the method of the present invention, there is no limitation to the method for applying an aqueous modified silk fibroin solution to the fabrics therefore, dipping method, spraying method, roller method, etc., can be used.

In order that good adhesion and uniform film formation of the modified silk fibroins can be imparted to the fabrics, a pretreatment of fabrics may be carried out such as alkali treatment of polyester fibers, acid treatment or low-temperature plasma treatment of nylon fibers by oxygen, nitrogen, air, argon, etc.

The fibers to which modified silk fibroins were applied are dried. By carrying out wet heat treatment, a stronger film can be formed. The wet heat treatment is carried out at 90°C or higher, preferably 110°C or higher.

In the modified silk fibroin-treated fabrics of the present invention, a uniformly thin film wraps the fibers, thus the modified silk fibroin film cannot be dissolved in water any longer, therefore it is resistant to laundering.

For the modified silk fibroin solutions used in the present invention, for the stabilization of the silk fibroin solutions, namely to prevent gumming up, a heteroprotein such as atherocollagen, hydrolyzed collagen, gelatin, casein, etc., may be added before or after reacting with CTA. The amount of the heteroprotein to be used is at most 30% of the silk fibroins. If it is greater than 30%, the film formability is poor and the appearance and hand are poor.

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If necessary, softening agents, antistatic agents, preservatives, color-adjusting agents, stabilizers, reaction catalysts, etc., may be added to the aqueous silk fibroin solutions used in the present invention.

Application examples

In the following, application examples will be used to explain the present invention concretely. In the application examples, "parts" means "parts by weight."

The weight increase in the application examples is defined by:

$$\text{Weight increase (\%)} = 100 \times ((\text{weight after treatment} - \text{weight before treatment}) / \text{weight before treatment})$$

The molecular weight of the silk fibroin was measured by high-performance liquid chromatography (HPLC) using a gel filtration column. The conditions for the HPLC were as follows:

Column: Asahipak G8-620

Eluant: 0.2M phosphoric acid buffer solution (pH 7.0)

Elution conditions: flow rate 1.0 mL/min.

Cytochromec, Ovalbumin, and Transferrin were used as standards.

Detection was carried out by measuring the absorbance at 280 nm.

Application Example 1

Spun silk waste was used as the raw material for silk fibroin. 100 parts of the spun silk waste were stirred and scoured at 95-98°C for 3 h in a solution made of 30 parts of

Marseilles soap and 3000 parts of water until the residual glue was reduced to less than 0.1%, and after washing with water, it was dried at 80°C with hot air.

100 parts of calcium chloride ($\text{CaCl}_2 \cdot 2 \text{H}_2\text{O}$) were mixed with 100 parts of water to prepare 200 parts of an aqueous 38 wt% calcium chloride solution, then the solution was heated to 110°C. Then 40 parts of scoured spun silk waste were added to the solution while stirring for 5 min using a kneader and then the mixture was stirred 30 min to complete dissolution.

Then 2000 regenerated cellulose hollow yarns (inner diameter: 200 μm , film thickness: 20 μm , length: 500 mm) were tied up in a bundle and both ends are fixed (sealed) without closing the holes of the hollow yarns to give a hollow fiber dialyzer, then the dialyzer was used and the above-mentioned dissolved solution was fed into it at a rate of 0.2 L/h, and deionized water was used for dialysis to give an aqueous fibroin solution. The fibroin concentration of the aqueous fibroin solution was 12 wt% and the residual calcium chloride was 0.001 wt%.

The molecular weight of the thus obtained silk fibroin measured by HPLC was approximately 150,000. 1000 parts of it were mixed with 10 parts of an aqueous 0.5 part [sic] sodium hydroxide solution and then the mixture was stirred and heated at 85°C for 5 h to hydrolyze the silk fibroin. The molecular weight of the silk fibroin after the hydrolysis was approximately 15,000. Then 25 g of 5% aqueous CTA solution were added dropwise to it over a period of 30 min with stirring. During this period, 0.01N sodium hydroxide was added dropwise to maintain the pH of the reaction system at 10. After completion of the dropwise addition of the CTA, it was further stirred for

2 h while the pH was maintained at 10 and it was allowed to stand overnight. Then 5 g of weakly acidic ion-exchange resin (trade name: Amberlite IRC-50) were added to neutralize to pH 6.8, and the sodium ions and a very small amount of unreacted CTA in the reaction system were removed. Then the ion-exchange resin was filtered to give 1050 parts of fiber treatment solution containing 11.5% pure cation-modified silk fibroin. After the determination of the amino nitrogen before and after reacting with CTA, it was found that at least 90% of the amino nitrogen had reacted.

Nylon taffeta with nylon multifilament 70 d/34 f, 106 warp yarns/in, and 84 filling yarns/in was used as an objective fiber, common methods were used for scouring, bleaching, and heat setting, then it was dipped in the 3 wt% aqueous solution of cation-modified silk fibroin previously prepared, then it was dewatered with a mangle to 100% pickup, dried at 120°C for 5 min, and subsequently was subjected to wet heat treatment at 110°C for 20 min.

The weight increase of thus obtained nylon taffeta was 2.94% and the unique slipperiness of nylon had disappeared, but it had a silky hand, with resilience, and the metallic luster had disappeared and it exhibited a silk-like luster, thus the nylon taffeta was modified to be silk-like.

Next, the modified nylon taffeta fabrics were laundered 10 times using a household detergent. The increase of weight after laundering was 2.80% and the retention of the modified silk fibroin was 95%, and there was no change in the appearance, hand and luster.

Comparative Example 1

Nylon taffeta fabrics were modified using the procedure of Application Example 1 except that the silk fibroin was not subjected to cation modification, but a hydrolyzed aqueous silk solution with molecular weight approximately 15,000 was used.

The increase of weight after dipping, dewatering, drying, and wet heat treatment was 2.90%. The unique slipperiness of nylon had disappeared but it had a silky hand with resilience, the metallic luster had disappeared, and it exhibited a silk-like luster, so the nylon taffeta was modified to be silk-like.

However, when the thus modified nylon taffeta was laundered 10 times using a household detergent, the increase of weight was 0.30% and the retention was 10%. The small amount of silk fibroin remaining after laundering adhered like a powder and there was no luster, so the quality was poor.

Application Example 2

The hydrolysis of silk fibroin was carried out using the procedure of Application Example 1, and by the increase or decrease of time, the CTA-modified aqueous silk fibroin solutions shown in Table I were obtained. In all the cases, more than 90% of the amino nitrogen reacted.

It was distilled to 3 wt% silk fibroin, and polyester taffeta with polyester multifilament 75 d/36 f, 106 warp yarns/in, and 87 filling yarns/in was used as an objective fiber to carry out the treatment of fibers using the procedure of Application Example 1. The results are shown in Table I. The

quality of the silk-like modification was evaluated by its silk-like luster and the appearance and hand.

Table I

① 絹フイブリン の分子重	② 洗濯前の 増量率 (%)	③ 洗濯前の 絹様改質 の品位	④ 洗濯10回 後の保持率 (%)	⑤ 洗濯10回 後の絹様改 質の品位
7000 (比較例) ⑥	205	△	88	×
8500	200	○	87	
10000	198	○	86	○
60000	201	○	84	○
85000	200	○	80	
150000 (比較例) ⑦	210	○	46	×

⑦ 註) ○: 非常に良好 ○: 良好 △: やや不良 ×: 不良

- Key: 1 Molecular weight of silk fibroin
 2 Increase of weight prior to laundering
 3 Grade of silk-like modification prior to laundering
 4 Retention after laundering 10 times
 5 Grade of silk-like modification after laundering 10 times
 6 Comparative example
 7 Notes, ⑥: Very good, ○: Good, △: Fair, X: Poor.

Table II

① CTA改質絹 フィブロイン 水溶液の濃度 (%)	② ピック アップ (%)	③ 洗濯前の 重量率 (%)	④ 洗濯前の 絹様改質 の品位	⑤ 洗濯10回 後の保持率 (%)	⑥ 洗濯10回 後の絹様 改質の品位
0.5 (比較例)	100	0.15	×	0.5	×
0.5 ⑦	100	0.61	○	0.6	△
5.0	50	2.47	○	0.6	○
5.0	100	4.88	○	0.6	○
11.5	100	11.11	○	0.4	○
20.0	100	20.10	○	0.2	△
25.0 ⑦	100	22.00	×	0.0	×

- Key: 1 Concentration of CTA-modified aqueous silk fibroin solution
 2 Pickup
 3 Increase of weight prior to laundering
 4 Grade (quality) of silk-like modification prior to laundering
 5 Retention after laundering 10 times
 6 Grade (quality) of silk-like modification after laundering 10 times
 7 Comparative example

As explained above, if the molecular weight of silk fibroin is less than 8500 (degree of polymerization 100) the silk fibroin films become fragile and powdery adhesion occurs on the surface of fibers, therefore the quality of silk-like modification is inferior, whereas if the molecular weight is greater than 150,000 (no hydrolysis) the adsorption sites per

unit molecular weight becomes small, so the laundering durability is poor.

Application Example 3

The procedure of Application Example 1 was followed and the concentration of the treatment solution and the amount of pickup were changed to investigate the relationship between the degree of treatment and the grade of the silk-like modification. The results are given in Table II.

Thus when the weight increase is less than 0.5%, it is the same as being untreated, so the silk-like modification is insufficient, whereas when it is greater than 20%, the treated fibers become coarse and hard.

Application Example 4

As an objective fiber, a fabric with No. 60 count spun cotton yarn, 90 warp yarns/in, and 88 filling yarns/in was used, and singeing, desizing, scouring, bleaching, mercerizing, and fixing were carried out using common methods. Two pieces were prepared, and an aqueous solution of 3 wt% of CTA-modified silk fibroin with molecular weight 15,000 was prepared using the procedure of Application Example 1 for carrying out the treatment of 200% pickup. On the one hand, (A) after treatment and drying of the first sample piece, it was subjected to wet heat treatment at 110°C for 20 min, and on the other hand, (B) another sample piece was not subjected to wet heat treatment. The results are shown in Table III.

Table III

	洗濯前の 増重率 ① (%)	洗濯前の 絹織改良 の品位 ②	洗濯10回 後の保存率 ③ (%)	洗濯10回 後の絹織 改良の品位 ④
A	6.55	◎	96	◎
B	5.89	◎	72	◎

- Key: 1 Weight increase prior to laundering
 2 Grade of silk-like modification prior to laundering
 3 Retention after laundering 10 times
 4 Grade of silk-like modification after laundering 10 times

Therefore, when wet heat treatment was not carried out, the resistance to laundering of the adsorbed silk fibroins is somewhat weak.

Effect of the invention

As described in detail above, the fabrics of the present invention treated with cation-modified silk fibroins exhibit the appearance, hand and luster of silk, and it is not a mere adsorption but an electrostatic adsorption, therefore strong dewatering of treated fabrics is possible. Therefore fiber-to-fiber adhesion of fabrics does not occur, thus the treatment of fibers is possible. For the same reason, the resistance to laundering is remarkably good.